Communications to the Editor

Linear Ferrocenylene−Siloxyl−Diacetylene Polymers and Their Conversion to Ceramics with High Thermal and Oxidative Stabilities

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The synthesis of ceramic materials by pyrolysis of polymer precursors is well established.[1] Although this approach has been used successfully for such materials as SiC, Si_3N_4, and BN, relatively little work has been reported on the pyrolysis of transition metal containing polymers. The conversion of organotransition metal polymers into ceramics could lead to materials with useful mechanical, electrical, and magnetic properties. Ferrocene-containing polymers are particularly attractive materials for the synthesis of iron-containing ceramics as the ferrocenylene moiety is thermally robust, relatively inexpensive, and readily derivatized.[2] Thus, the study of ferrocene polymers continues to be an active area.[3] Reports on the formation and properties of Fe−Si−C ceramics from pyrolysis of organoiron polymers have recently appeared.[4] It should also be noted that Yajima reported the formation of iron-containing glassy carbon obtained from the pyrolysis of ferrocene resins as early as 1977.[4f]

Polymers containing diacetylene groups have received considerable attention.[5] However, incorporation of transition metal complexes into diacetylene polymers has been limited to a few examples, including 1,1′-ferrocenylene-containing polymers.[4d−e] These latter materials exhibit a high char yield on pyrolysis but require the synthesis of a derivatized ferrocene. Research in our group has focused on the synthesis of diacetylene polymers for use in high-temperature applications.[6] These studies have shown that pyrolysis of polymers containing silicon and boron yields materials with excellent thermal and oxidative stabilities. In this paper we report our study on the synthesis and thermal properties of a ferrocenylene−siloxyl−diacetylene polymer containing *m*-carborane units in the polymer backbone.

The synthesis of the new ferrocenyl−siloxyl−carboranyl−diacetylene polymer is shown in Scheme 1. The reaction of dilithiobutadiyne[7] (**3**) with 1,7-bis(chlorotetramethyldisiloxyl)-*m*-carborane (**4**, 2 equiv) followed by treatment with dilithioferrocene−tmeda[8] (**5**, 1 equiv) gave the desired polymer (**1**). The product is a tacky, brown solid that is soluble in common organic solvents and can be stored under ambient conditions for months with no apparent change in properties. The progress of the reaction can be easily monitored by infrared spectroscopy.[9] GPC measurements show this material has a molecular weight of approximately 10 000 relative to polystyrene. This corresponds to 9−10 repeat units in the polymer.

Infrared spectroscopy (KBr) showed a strong B−H stretch at 2596 cm^{-1} verifying the presence of the *m*-carboranyl groups (Figure 1). The butadiyne stretch appears at 2170 cm^{-1}. Bands at 2962, 1260, and 1075 cm^{-1} are assigned to C−H, Si−C, and Si−O bonds of the tetramethyldisiloxyl linkages, respectively. A band at 3092 cm^{-1} is attributed to the C−H stretches of the 1,1′-ferrocenylene groups. The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with a polymer structure in which 1,7-bis(tetramethyldisiloxyl)-*m*-carborane units are randomly separated by 1,1′-ferrocenylene and diacetylenic groups. The ^1H NMR (300 MHz, $CDCl_3$) spectrum of **1** showed resonances at 0.34, 0.27, 0.22, and 0.10 ppm for the siloxyl methyl groups. The 1,1′-ferrocenylene proton resonances appeared at 4.25 and 4.05 (major peaks) with smaller peaks of approximately equal intensity at 4.35, 4.30, 4.16, and 4.11 ppm. The B−H protons appear as a series of broad signals between 1.0 and 3.5 ppm. The $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) spectrum of **1** showed the siloxyl methyl groups at 0.62, 0.55, 0.48, and 0.30 ppm, the 1,1′-ferrocenylene carbon resonances at 72.97 (minor), 72.83, 71.67, 71.60 (minor), and 71.12 ppm, and the carboranyl carbon shifts at 68.31 and 67.90 (minor peak) ppm. The diacetylenic carbons appear as two small singlets at 87.0 and 84.6 ppm.

Heat treatment of the polymer to 350 °C under an inert atmosphere results in the formation of a black, elastomeric thermoset with 98% weight retention. A small amount of shrinkage was observed during the formation of the thermoset. The elastomeric nature of the thermoset is in contrast to the hard, tough thermosets obtained from siloxyl−diacetylene polymers such as poly(tetramethyldisiloxyl−diacetylene).[6b] Further heating of the thermoset to 1000 °C under N_2 affords a hard, black ceramic in 78% ceramic yield.[10] The ceramic char is attracted to a bar (permanent) magnet, indicating ferromagnetic behavior which is currently under investigation.

Thermogravimetric analysis (TGA) of **1** showed this material to have excellent thermal and oxidative stabilities (Figure 2). Heating a sample of the polymer to 1000 °C (10 °C/min) under N_2 gave a weight retention of 78% with the onset of weight loss at approximately 380 °C. This thermal stability can be compared to that of other siloxyl−ferrocenylene polymers that have shown 50% or less weight retention under similar conditions.[11] The oxidative stability of the resulting char was found to be excellent. Heating a sample (10−20 mg pieces) of the polymer char to 1000 °C (10 °C/min) in air resulted in essentially no weight loss (Figure 2). The sample appears to maintain its magnetic character after such treatment. The high oxidative stability of the polymer char is attributed to the presence of boron in the material. The stabilizing effect of boron in oxidizing

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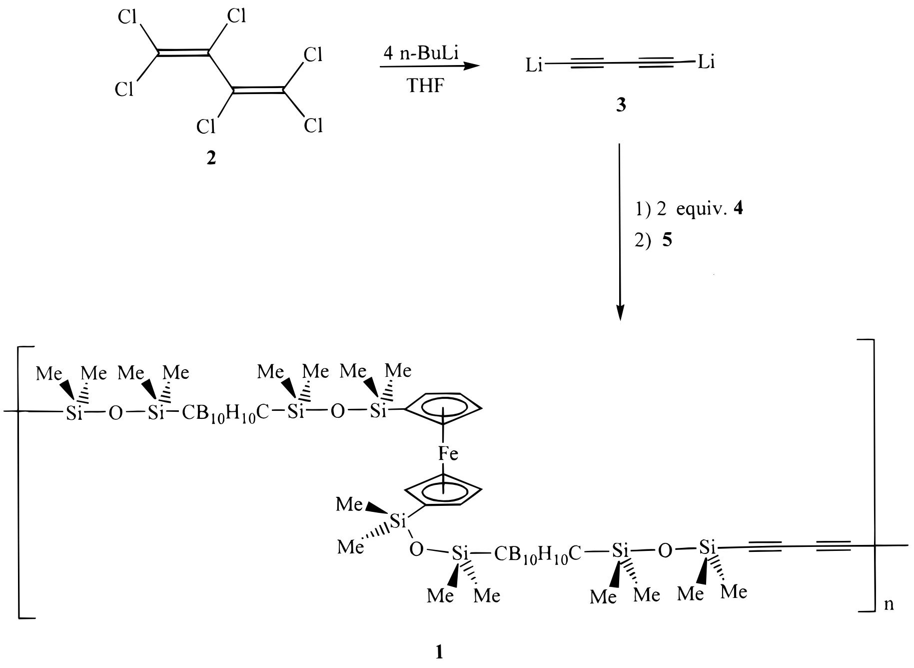
Scheme 1



4 = 1,7-bis($ClMe_2SiOMe_2Si$)-m-$C_2B_{10}H_{10}$

5 = $(LiCp)_2Fe$ · TMEDA

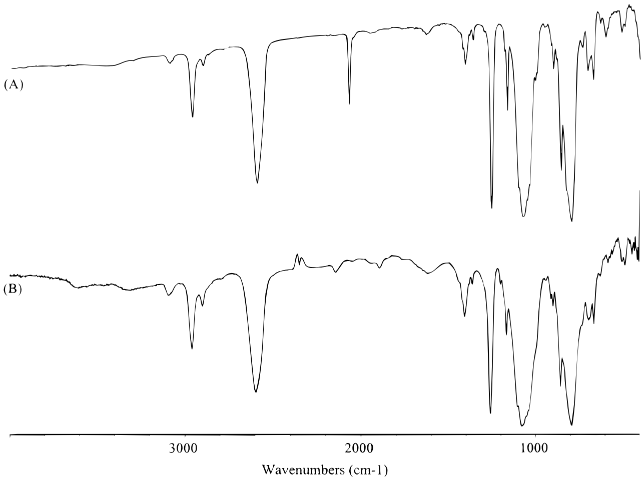


Figure 1. FTIR spectra (KBr) of **1** (A) and thermoset obtained from heat treatment of **1** to 450 °C (B).

environments is well-known for carbon-based materials.[12] Previous thermal (TGA) studies on 1,1′-ferrocenylene−siloxyl polymers have shown these materials to have weight retentions of only 40−50% at 700 °C (10 °C/min, N_2).[6] On further heating, a second decomposition process beginning at 1350 °C resulted in a final weight retention of 74%. Elemental analysis showed this latter material to be similar to samples that were prepared at 1000 °C but with slightly less silicon.[8]

Differential scanning calorimetry (DSC) studies on **1** revealed an exotherm centered at 380 °C. This exotherm is attributed to the cross-linking reaction of the butadiyne groups. This assignment is supported by the disappearance of the exotherm on subsequent DSC scans and by the loss of the butadiyne stretch (2170 cm^{-1}) in the infrared spectrum of polymer samples heated above 350 °C (Figure 1).

The formation of iron-containing ceramics was achieved using preceramic ferrocenylene polymers. These polymers can be obtained in high yield from a two-pot reaction sequence. The incorporation of diacetylene groups into the polymer backbone provides a suitable cross-linking site such that the linear polymer to thermoset to ceramic conversions proceed in high yields. The incorporation of boron into the polymer backbone imparts high oxidative stability to the polymer chars. The magnetic and electrical properties of the ceramic product obtained from pyrolysis of the polymer are currently under investigation.

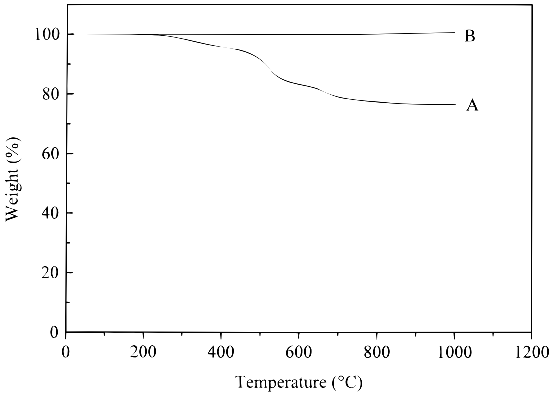


Figure 2. TGA of **1** under N_2 (A) and the Resulting Char in Air (B).

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(9) In a typical experiment, a solution of THF (10 mL) and *n*-BuLi (10.2 mL of 2.5M) in a 250 mL Schlenk flask was stirred at −78 °C. The solution was treated with hexachlorobutadiene (1.0 mL, 6.38 mmol) dropwise over a period of 10 min. The cold bath was removed and the solution was stirred at room temperature, giving a gray-brown slurry. After stirring for 2 h at room temperature, the slurry of dilithiobutadiyne was transferred via cannula to a flask containing a THF solution (10 mL) of 1,7-bis(chlorotetramethyldisiloxyl)-*m*-carborane (6.10 g, 12.77 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 30 min, giving a brown solution. The solution was cooled to 0 °C and treated with a slurry of $Li_2Cp_2Fe \cdot tmeda$ (2.0 g, 6.38 mmol) in 20 mL of THF, which was added via cannula. The reaction mixture was stirred at room temperature for 1 h. Measurement of an FTIR spectrum of the crude reaction mixture showed the presence of small and variable amounts of terminal butadiyne groups (2140 cm^{-1}). These groups were found to be undesirable as they slowly cross-link at room temperature, giving an insoluble material. Thus, when these groups were observed, they could be coupled by addition of 2−3 drops of 1,7-bis(chlorotetramethyldisiloxyl)-*m*-carborane. The reaction was quenched by addition of cold aqueous NH_4Cl. After aqueous workup and extraction with diethyl ether, the orange-brown organic polymer solution was dried over $MgSO_4$, filtered, and the solvent removed in vacuo to give a viscous brown oil. The oil was further dried by heating for several hours in vacuo at 70 °C. This gave 5.63 g (84%) of a tacky, brown solid. Anal. Calcd (Found): C, 39.05 (39.19); H, 7.33 (7.57); Si, 21.49 (24.60); B, 20.68 (17.87); Fe, 5.34 (5.43).

(10) Elemental analysis of char obtained from heat treatment of **1** to 1000 °C: C, 35.66; H, 0.0; Si, 21.67; B, 20.25; Fe, 4.89. Elemental analysis of char obtained from heat treatment of **1** to 1500 °C: C, 35.67; H, 0.0; Si, 20.20; B, 20.44; Fe, 4.87.

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