Synthesis and Characterization of Poly(carborane–siloxane–acetylene)

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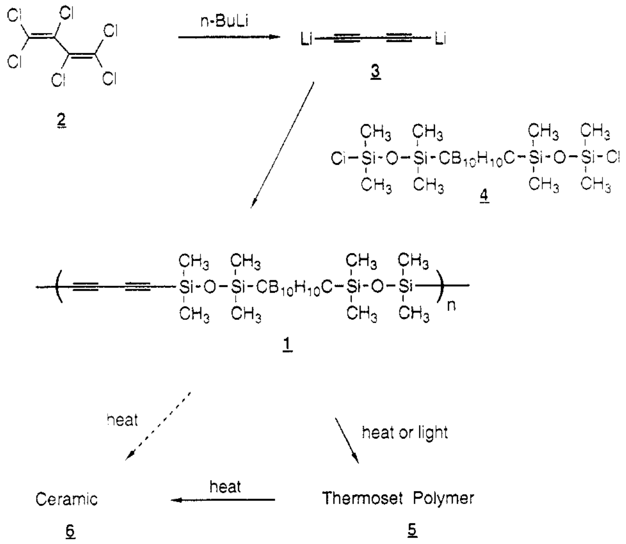
Inorganic–organic hybrid polymers represent a very active area of current research activities, which has considerable potential for providing new advanced materials. In our continuing interest in high-temperature polymers and polymeric precursors for ceramics, we are especially interested in polymers containing boron, silicon, and acetylene moieties. Numerous polymers containing carborane cage structures have been reported.[1–5] Polymers containing the carborane unit within the backbone exhibited appreciable enhancement in their thermal stability. The development of carborane–siloxane polymers in the early 1960s was a major breakthrough in the search for high-temperature elastomers. These elastomeric materials show superior thermal and oxidative stability at elevated temperatures compared to siloxane-based polymers.[6,7] The carborane-containing systems retained their elastomeric properties after aging in air at 315 °C for 300 h.[8] Because of the superior thermal and oxidative stability of the poly(carborane–siloxane) elastomers, we have studied the effects of incorporating acetylenic units into the structure for cross-linking purposes. The presence of acetylenic units in the backbone of a polymeric material provides many attractive advantages. The acetylene remains dormant during processing under ambient conditions. During reaction by thermal or photochemical means, a conjugated cross-link is formed by an addition polymerization reaction without the formation of volatile byproducts.

We report the development of a successful route to poly(carborane–siloxane–acetylene)s, a new class of inorganic–organic hybrid polymers, which exhibit outstanding thermal and oxidative properties and can be easily processed into shaped configurations (see Scheme 1). A recent method for preparing silylene–diacetylene polymers via dilithioacetylenes was adapted for the synthesis of these hybrid polymers.[9,10] The synthesis of 1 is a one-pot, two-stage reaction. Dilithiobutadiyne (3) is generated by reacting hexachlorobutadiene (2) in THF with 4 equiv of *n*-butyllithium at −78 °C. The reaction is allowed to warm to ambient temperature and then recooled to −78 °C. Equal molar amounts of dilithiobutadiyne and 1,7-bis(chlorotetramethyldisiloxy)-*m*-carborane (4), purchased from Dexil Corp., were reacted to generate the linear polymer 1 in high yield. Molar calculations were based on 3 being formed quantitatively. After the addition of 4, the reaction mixture was allowed to slowly warm to room temperature. The reaction mixture was then poured into dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with water until neutral and dried over anhydrous sodium sulfate. The ether was removed at reduced pressure to afford a dark brown, viscous liquid 1 in quantitative yield. The polymer 1 is soluble in most common organic solvents. GPC analysis indicated the presence of low molecular weight species (≈500) as well as higher average molecular weight polymers ($M_w \approx 4900$, $M_n \approx 2400$), averaging to about 10 repeat units. Heating of 1 at 150 °C under reduced pressure removed lower molecular weight polymeric species, leaving a 92–95% overall yield. An FTIR study of 1 shows the presence of prominent absorptions at 2963 (C–H), 2600 (B–H), 2175 ($C\equiv C$), 1260 (C–Si), and 1081 (Si–O) cm^{-1}. Internal alkynes often have very weak or nonexistent transitions, but the 2175-cm^{-1} transition is as intense as the other vibrational absorptions of 1 (see Figure 1).

Scheme 1



The liquid linear polymer 1 is readily converted into a thermoset under thermal conditions. Polymers containing aromatic or heteroaromatic rings and acetylenic units in the backbone have been reported[10–13] to undergo cross-linking to form network polymers above 150 °C. A shiny void-free dark brown solid 5 was produced by thermally curing 1 at 300, 350, and 400 °C for 2 h at each temperature either under inert conditions or in air. Gelation occurred during the initial heat treatment at 300 °C. An FTIR spectrum of 5 shows the disappearance of the acetylenic absorption at 2175 cm^{-1} and the appearance of a new, weak peak centered at 1600 ($C=C$) cm^{-1}. A spectrum of 5 cured in air also exhibited an absorption at 1714 cm^{-1}, attributed to a carbonyl group. The other characteristic peaks were still present. Pyrolysis of 5 to 1000 °C yielded a black solid ceramic material 6 in 85% yield. The characteristic FTIR absorptions of 1 and 5 were now missing.

Differential calorimetric (DSC) analyses were run on 1 from 30 to 400 °C in both nitrogen (see Figure 2) and air. Similar results were obtained regardless of the atmosphere. A small broad exotherm was apparent from about 150 to 225 °C and was attributed to the presence of a small amount of primary terminated acetylenic units. This peak was absent for 1 heated at 150 °C for 30 min. A larger broad exotherm commencing at 250 °C and peaking at 350 °C was attributed to the reaction of the secondary acetylene units to form the cross-link. This exotherm was absent after heat treatment of 1 at 320 and 375 °C for 30 min.

The thermal and oxidative stability of 1 and its conversion into 5 and 6 were studied by thermogravimetric analysis (TGA). The TGA studies were determined between 50 and 1000 °C at a heating rate of 10 °C/min in both argon and air atmospheres. Upon heating to 1000 °C in argon, 1 exhibited a ceramic yield of 85%. When the ceramic material 6 was cooled back to 50 °C and rescanned to 1000 °C in air, the sample gained weight (≈2%) attributed to oxidation. A TGA thermogram of 1 heated to 1000 °C in air, which was initially converted into 5, showed less weight loss relative to pyrolysis under inert conditions and exhibited a ceramic yield of 92%.

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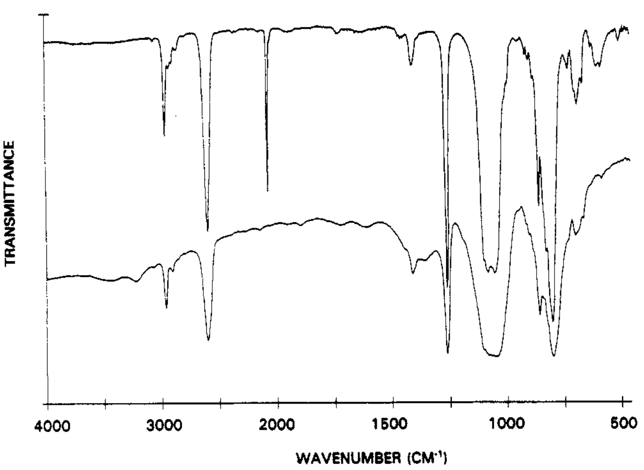

Figure 1. FTIR spectra: film of 1 on a NaCl disk (top) and a KBr pellet of 5 (bottom).

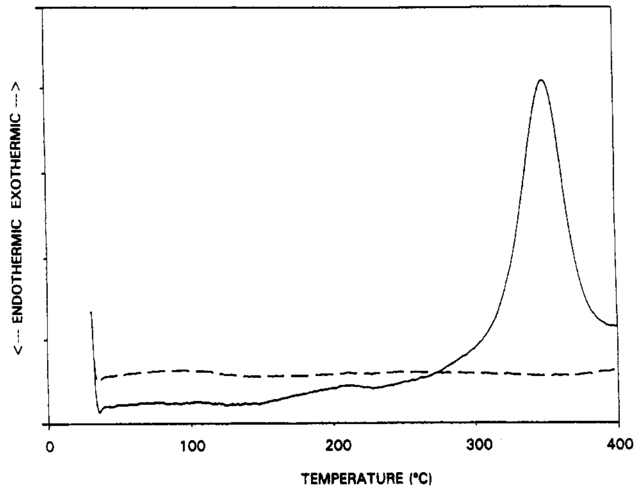

Figure 2. DSC thermograms of 1 (solid line) and cured 5 (dash line).

Further TGA studies of the ceramic 6 in air revealed that additional weight loss did not occur and that the sample actually increased in weight as observed previously. Furthermore, a sample that had been heated to 1000 °C in air, cooled, and then rerun in argon showed no weight changes. Scanning electron microscopic (SEM) and scanning auger microprobe studies show that a protective film composed mostly of silicon oxide forms on the outer surface of 5 and 6 upon exposure to high temperatures in air.[14] This film protects the bulk of the sample against oxidation.

The pyrolysis of 5 in a stream of argon to 900 °C at 10 °C/min afforded a black component 6 in 85% ceramic yield that retained its shape except for some shrinkage. Elemental analysis of the pyrolysis product gave 22.76% B, 23.70% Si, 35.06% C, and 0.43% H. Thus, the ceramic material contains a large excess of carbon (compare calculated values for B_4C and SiC, respectively: 78.26% B, 21.74% C and 70.04% Si, 29.96% C). This was not unexpected since it is known that ceramics formed from pyrolysis of polymers containing unsaturated organic groups attached to silicon, which makes them less likely to be cleaved, have high carbon levels.[13,16] Our exploratory experiments show polymer 1 to be potentially useful as a binder or matrix material for advanced composites and in the formation of shaped ceramic bodies.

In summary, carborane–siloxane–acetylenic-based thermosetting polymers are designed to take advantage of the inorganic–organic hybrid approach to produce high-temperature polymers and ceramic-based materials. Polymer 1 possesses exceptional thermal and oxidative stability, is a viscous liquid that is soluble in most organic solvents, and is easy to process thermally into structural components. Thermal cross-linking occurs through the triple bonds to produce the thermoset 5. Thermoset 5, in turn, produces a ceramic material 6 in high yield (85% and 92%, respectively) upon pyrolysis in nonoxidizing and oxidizing environments. When heated in an oxidizing environment, 6 actually gained weight. The potential utility of polymer 1 as a matrix material for advanced composites and further conversion into a shaped ceramic component is due to the ease of processability, high ceramic yield, oxidative stability, and retention of its structural integrity at elevated temperatures. Further studies are underway to fully evaluate the thermal properties of 5 and 6 and to develop new chemistries pertaining to the design of high-temperature polymeric materials and ceramics.

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References and Notes

(1) Colquhoun, H. M.; Daniels, J. A.; Stephenson, I. R.; Wade, K. *Polym. Commun.* **1991**, *32*, 272.
(2) Williams, R. E. *J. Pure Appl. Chem.* **1972**, *29*, 569.
(3) Papetti, S.; Schaeffer, B. B.; Gray, A. P.; Heying, T. L. *J. Polym. Sci., Polym. Chem. Sci.* **1966**, *4*, 1623.
(4) Green, J.; Moyes, N.; Cohen, M. S. *J. Polym. Sci., Polym. Chem. Sci.* **1964**, *4*, 3113.
(5) Alexander, R. P.; Schroeder, H. *Inorg. Chem.* **1963**, *2*, 1107.
(6) Peters, E. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *C17* (2), 173.
(7) Papetti, S.; Schaeffer, B. B.; Gray, A. P.; Heying, T. L. *J. Polym. Sci., Polym. Chem. Sci.* **1966**, *4*, 1623.
(8) Peters, E. N.; Hedaya, E.; Kawakami, J. H.; Kwiatkowski, G. T.; NcNeil, D. W.; Tulis, R. W. *Rubber Chem. Technol.* **1975**, *48*, 14.
(9) Ijadi-Maghsooke, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485.
(10) Ijadi-Maghsooke, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.
(11) Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3530.
(12) Neenana, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3525.
(13) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3528.
(14) Pehrsson, P. E.; Henderson, L. J.; Keller, T. M., manuscript submitted to *Chem. Mater.*
(15) White, D. A.; Oleff, S. M.; Fox, J. R. *Adv. Ceram. Mater.* **1983**, *2*, 53.
(16) Burns, G. T.; Taylor, R. B.; Xu, Y.; Zangvil, A.; Zank, G. A. *Chem. Mater.* **1992**, *4* (6), 1313.