Macromolecules **1996,** *29,* 3647−3650 **3647**

Synthesis and Characterization of Linear Boron−Silicon−Diacetylene Copolymers

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Received September 29, 1995
Revised Manuscript Received February 13, 1996

Introduction

Rapid progress in modern technologies has created a significant demand for processable materials that can be converted into shaped components having high thermal and oxidative stabilities.[1−4] Current commercial organic-based systems are limited to use temperatures below 300 °C.[1−5] The incorporation of inorganic elements into an organic polymeric system has the potential for extending these temperature limitations, in addition to enhancing properties such as hardness, chemical inertness, processability, and solubility.[6−9] Previous work in our group has focused on the inorganic−organic hybrid approach to prepare carborane−siloxane−acetylene polymers and copolymers.[10−12] Acetylenic-based materials can react either thermally or photochemically to form conjugated polymeric cross-linked networks through an addition reaction without the evolution of volatiles.[5,13−15] Polysiloxanes possess high thermal stabilities, exhibit hydrophobicity, are flexible, and have low melting and/or softening points.[16−18] Carborane ($HCB_{10}H_{10}CH$)-containing polymers have remarkable chemical and thermal properties and exhibit good protection against oxidative degradation.[18−22] In our studies, we found that the thermal and oxidative properties obtained with carborane-based hybrid systems were outstanding compared to commercial organic systems.[10−12]

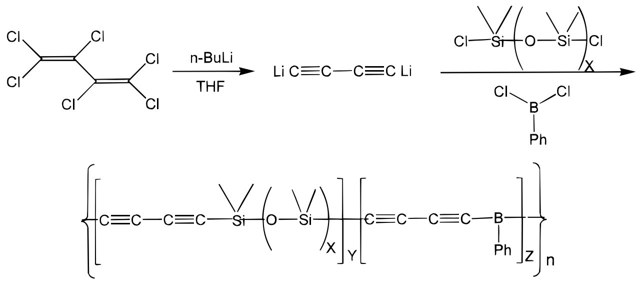
The relative high cost and current limited supply of carboranes pose significant difficulties for the utilization and development of polymers and ceramics based on carborane units. Thus an alternate source of boron was sought. Based on these factors, it was of interest to investigate polymeric systems containing acetylenic, siloxane/silane $\{Si(Me_2)[OSi(Me_2)]_x, x = 0,1,2\}$ and boron (BPh) moieties. The synthesis and properties of these copolymers are described in this note.

Experimental Section

All reactions were performed under inert conditions using standard Schlenk line techniques. THF was distilled from benzophenone/sodium prior to use. All chemicals were obtained from Aldrich Chemical Co. and were used as received. Thermogravimetric analyses (TGA) and differential scanning calorimetric analyses (DSC) were performed on a DuPont 951 module and a DuPont 910 calorimeter, respectively, equipped with a DuPont 2100 thermal analyzer. All thermal analyses were performed using heating rates of 10 °C/min under air or nitrogen atmospheres with flow rates of 50 cm³/min. Infrared spectra (FTIR) were obtained using a Nicolet Magna 750 spectrometer. ^1H and ^{13}C NMR were performed on a Bruker AC-300 spectrometer. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc.

Polymer Syntheses. A flame-dried 100 mL round-bottomed flask, connected to an argon source, was equipped with a magnetic stirbar and septum. Tetrahydrofuran (THF; 8 mL) was injected and the flask placed in a dry ice/acetone bath (∼−78 °C). *n*-Butyllithium (BuLi, 10.2 mL of a 2.5 M hexane solution, 26.4 mmol) was then added slowly and the mixture stirred for ∼5 min. Hexachlorobutadiene (0.99 mL, 6.2 mmol) was then introduced dropwise via syringe over a 10 min period, with stirring. After complete addition, the reaction mixture was stirred at −78 °C for 5−10 min, the cold bath was then removed, and the reaction mixture was stirred at room temperature for 2.5 h to afford a brown mixture.[23] Meanwhile, a THF solution of dimethyldichlorosilane (DMS; 0.62 mL, 5.01 mmol) and phenylboron dichloride (PBD; 0.20 mL, 1.41 mmol) in THF was prepared at −78 °C. To this THF solution of PBD and DMS was added via cannula the brown mixture containing Li_2C_4. After complete addition, the reaction mixture was allowed to warm to ambient temperature, stirred 0.5 h, and then quenched with cold aqueous ammonium chloride. Following cold aqueous workup and extraction with ether, the product was separated and concentrated under reduced pressure at 85 °C to afford **1a**, 83% yield of a yellow solid. Copolymers **1b**−**d** were similarly prepared using siloxane to boron reagents as follows: **1b**, tetramethyldisiloxane (TMDS; 1.15 mL, 5.644 mmol), PBD (0.09 mL, 0.636 mmol); **1c**, TMDS (1.00 mL, 4.91 mmol), PBD (0.20 mL, 1.41 mmol); **1d**, hexamethyltrisiloxane (HMTS; 1.53 mL, 5.50 mmol), PBD (0.09 mL, 0.636 mmol). Dark brown products were obtained, with yields in the 80−85% range.

Scheme 1. Synthesis of Boron−Silicon−Diacetylene Hybrid Copolymers 1a−d



	X	Y	Z
1a	0	0.8	0.2
1b	1	0.8	0.2
1c	1	0.9	0.1
1d	2	0.9	0.1

Results and Discussion

The synthesis of boron−silicon−diacetylene copolymers **1a**−**d** is summarized in Scheme 1. The mole percent ratios of silane/siloxane (DMS, TMDS, and HMTS) to boron (PBD) reported in this paper are 90:10 and 80:20. Attempts to synthesize copolymers with other siloxane to boron ratios (40:60 and 50:50) resulted in only low molecular weight materials being isolated. The isolated copolymers (**1a**−**c**) were solids at room temperature whereas **1d**, containing the trisiloxane group, was a viscous liquid. Molecular weight determinations using polystyrene as standard were performed only on the trisiloxane copolymer (**1d**) and were found to be in the 2300 g/mol range. We were unable to completely dissolve copolymers **1a**−**c** in THF.

The structures of the copolymers were confirmed by FTIR spectroscopy, which showed strong acetylenic stretching (2070 cm^{-1}), strong Si−O−Si stretching (1070 cm^{-1}), and strong Si−C deformation (1270, 840, and 810 cm^{-1}) absorptions, as shown in Figure 1. The presence of trace amounts of terminal acetylenic end groups was indicated by a small absorbance at 3300 cm^{-1}. The presence of boron was confirmed by an absorbance at 1450 cm^{-1} (B−Ph). The presence of B−OH end groups or hydrolysis by-products was indicated by small absorbances in the 1345−1335 cm^{-1} region. When a sample of **1a** was heated to 400 °C and the residue analyzed by FTIR spectroscopy, acetylenic absorptions were not observed in either the 3300 or 2070 cm^{-1} region. Thus,

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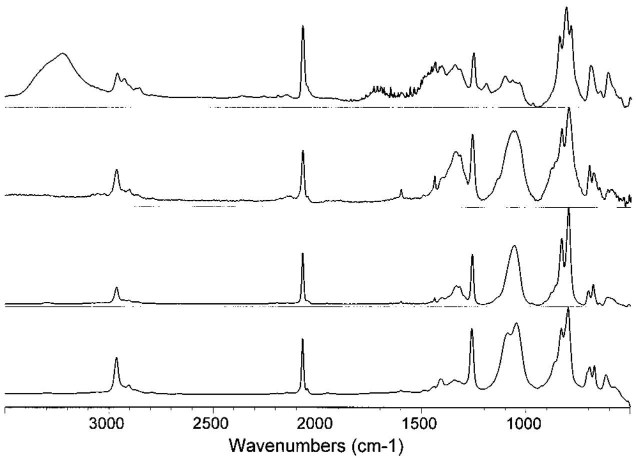

Figure 1. FTIR spectra (absorbance) of hybrid copolymers **1a** (top), **1b** (upper middle), **1c** (lower middle), and **1d** (bottom).

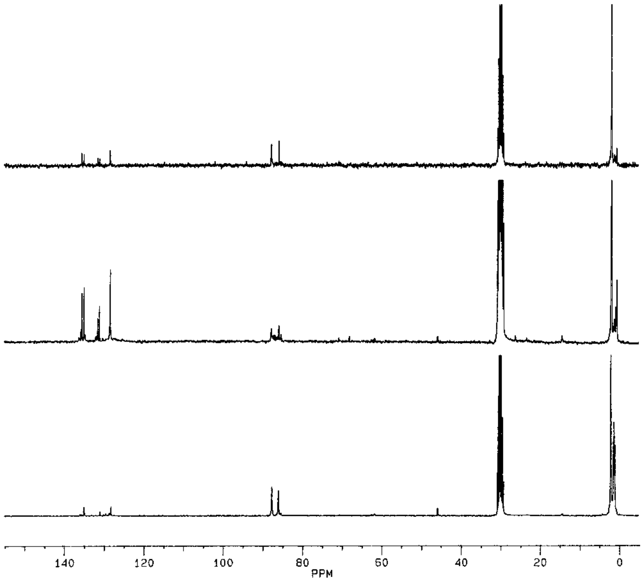

Figure 2. ^{13}C NMR (acetone-d_6) spectra of hybrid copolymers **1b** (top), **1c** (middle), and **1d** (bottom).

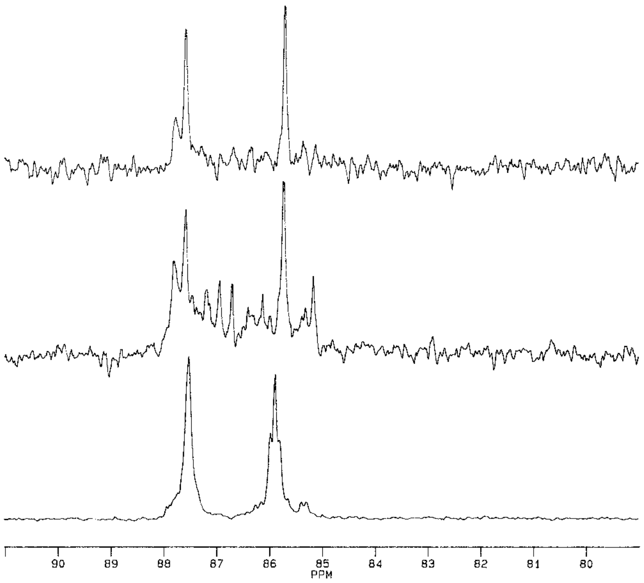

Figure 3. ^{13}C NMR (acetone-d_6) spectra showing the acetylenic region of hybrid copolymers **1b** (top), **1c** (middle), and **1d** (bottom).

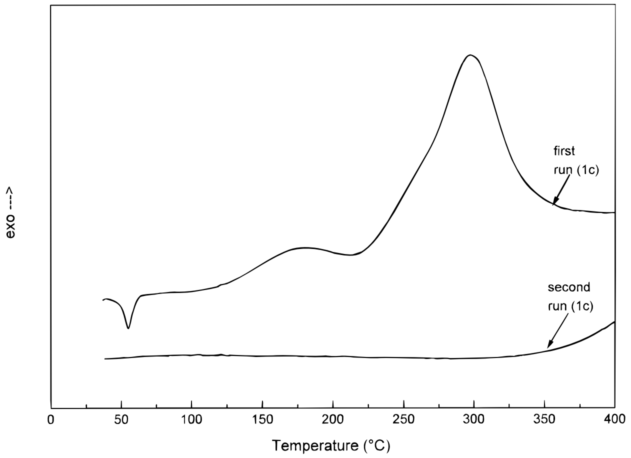

Figure 4. DSC thermograms of hybrid copolymer **1c** heated under a nitrogen atmosphere to 400 °C ("second run").

heating to 400 °C is interpreted as an adequate enough temperature for conversion of the acetylenic units into a cross-linked system.

Structural confirmations were also obtained by NMR analyses (see Figures 2 and 3). ^{13}C NMR confirmed aromatic carbons (B−Ph) by peak resonances with chemical shifts in the 135−127 ppm range. Acetylenic carbons were identified by peak resonances in the 88−85 ppm region while silylmethyl carbons were observed in the 2−0 ppm region. Splitting of the peaks in the acetylenic region suggests a combination of random microstructure and end group effects. ^{1}H NMR integration and chemical shifts were in agreement with ^{13}C NMR and FTIR interpretation. Elemental analysis data were in general agreement with calculated values.[24] The presence of some end groups and/or hydrolysis byproducts can explain slight discrepancies in the data. Elemental analysis variations for these systems are not uncommon.[25]

The copolymers displayed thermal characteristics typical of diacetylenic systems. DSC analyses of **1a**−**d** to 400 °C under inert conditions showed exotherms having onsets in the 200−225 °C temperature range and peak maxima in the 285−300 °C range. These exotherms were interpreted as the reaction of the internal diacetylenic functionalities. Small exotherms (5−10% of main exotherm) were also observed with peak maxima around 165 °C and were attributed to reaction of trace quantities of terminal acetylenic moieties. Thermal treatment of a copolymer at 160 °C for 2−5 min resulted in the disappearance of the small exotherm. Further analysis of the residues via a second DSC run showed featureless thermograms, indicating no further cross-linking attributed to the acetylenic functionalities and hence completeness of the initial reaction. Only copolymer **1c** displayed a melting point at 55.4 °C (see Figure 4) while no melting/softening transitions were observed for the copolymers **1a** and **1b**. Copolymer **1d** is a viscous liquid at room temperature.

Figure 5 shows TGA thermograms of copolymers **1a**−**d**. Char yields of 77.4, 75.0, 72.1, and 44.4% were obtained for **1a**−**d**, respectively. The char yields observed decreased with increasing siloxane spacer group length, DMS (**1a**: 77.4 wt %), TMDS (**1b** and **1c**: 75.0 and 72.1 wt %), and HMTS (**1d**: 44.4 wt %). This is consistent with reported trends that increasing the siloxane spacer group length lowers the thermal stabilities of the resultant polymeric systems.[12,13] Oxidative stability determinations were obtained by heating the charred residues in air to 1000 °C and monitoring the

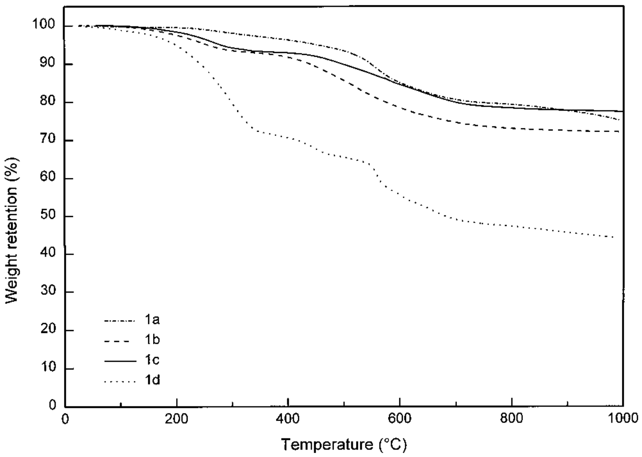

Figure 5. TGA thermograms of hybrid copolymers **1a**–**d** heated to 1000 °C under a nitrogen atmosphere at 10 °C/min.

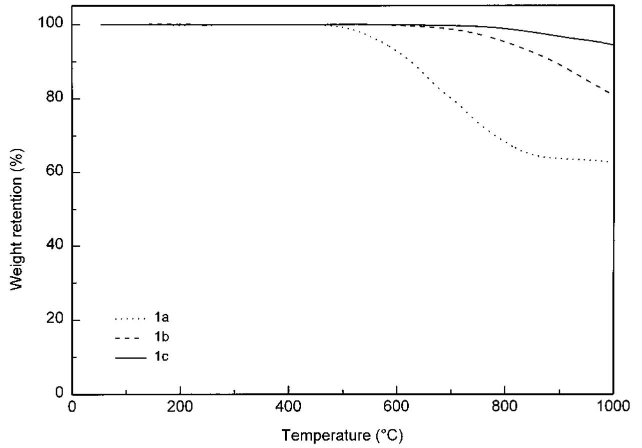

Figure 6. TGA thermograms of the chars obtained from hybrid copolymers **1a**–**c** heated to 1000 °C under an air atmosphere at 10 °C/min.

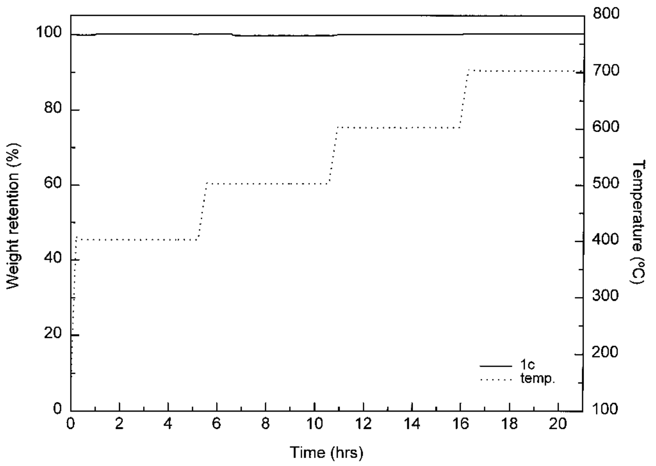

Figure 7. TGA of the ceramic obtained from hybrid copolymer **1c**, showing weight retention (solid line) when the sample was aged at 400, 500, 600, and 700 °C for 5 h, respectively (dotted line).

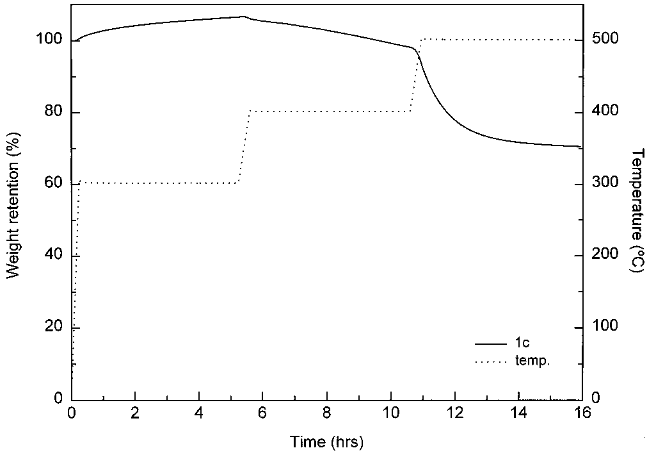

Figure 8. TGA of the thermoset obtained from hybrid copolymer **1c**, showing weight retention (solid line) when the sample was aged at 300, 400, and 500 °C for 5 h, respectively (dotted line).

weight retained. Weight residues of 63.8, 94.7, and 81.3% were obtained for copolymers **1a**–**c**, respectively (see Figure 6). Oxidative stability determinations were not performed on the residue from copolymer **1d** due to the low initial char yield of 44.4%, obtained under inert conditions.[12,13] When the char of **1c** was aged in sequence at 400, 500, 600, and 700 °C in air for 5 h, respectively, no weight losses for any of the aging segments was observed (see Figure 7).

A thermoset was prepared from **1c** via a controlled heat/isotherm profile under inert conditions. The thermoset, which was exposed to a maximum temperature of 550 °C, was aged in air at 300, 400, and 500 °C for 5 h at each temperature, respectively (see Figure 8). No weight losses were observed for the thermoset aged at 300 and 400 °C. In fact, a slight weight gain is observed and is attributed to the surface oxidation of silicon to silicon oxide and boron to boron oxide (B_2O_3). Aging at 500 °C resulted in a weight loss of 30% but constant weight was achieved at the end of the heat treatment, indicating that a protective layer had formed, which protects the bulk interior part of the polymer against further oxidation.

Summary

In summary, boron–silicon–diacetylenic copolymers were synthesized and characterized. These diacetylenic copolymers having various ratios of silane/siloxane and boron were evaluated for thermal and oxidative properties. The diacetylenic functionalities were found to cross-link thermally to give stable networks at elevated temperatures. The effects of silicon and boron incorporated into the host diacetylenic polymers were found to enhance their oxidative stabilities. Aging studies, performed on a thermoset and a ceramic residue and prepared from hybrid copolymer **1c**, showed these materials to have exceptional oxidative stabilities. Thus, these hybrid polymers show promise as materials for applications requiring high-temperature stability.

Acknowledgment. Support for this work was provided by the Office of Naval Research. R.A.S. is very grateful to The American Society for Engineering Education (ASEE) for providing his Postdoctoral Fellowship. The authors are grateful to Dr. Tai Ho of George Mason University for his assistance with the GPC measurements.

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