# Dependence of Thermal Properties on the Copolymer Sequence in Diacetylene-Containing Polycarboranylenesiloxanes

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Diacetylene-containing polycarboranylenesiloxane copolymers were prepared by two different methods to yield either alternating or block copolymers with respect to the diacetylene distribution along the backbone. With each method, a set of copolymers was prepared with trisiloxane:carborane:diacetylene molar ratios of 10:9:1, 5:4:1, and 3:2:1. Both sets of copolymers yielded networks upon thermal curing. Even though the two methods produced materials of comparable molecular weights and overall compositions, the variation in the copolymer sequence caused noticeable differences in the calorimetric glass transitions for the copolymers in which the diacetylene group was most concentrated (i.e., the 3:2:1 and 5:4:1 copolymers). The copolymers were characterized by differential scanning calorimetry, thermogravimetric analysis, and $^1$H solid-state NMR spectroscopy.

High-temperature elastomeric materials are required in the aerospace and defense industries for applications in sealing assemblies of landing gears for flight control and fuel systems, and for cable insulations. The demand for such materials also exists for resist layers in the manufacture of computer chips. Polymers containing siloxane and carborane groups exhibit exceptional thermal and thermo-oxidative properties.[1−5] These high-temperature polymers can be made elastomeric by vulcanization in air at 315 °C for 300 h; the cross-linking takes place through vinyl groups introduced with methylvinylsiloxane units in the backbone.[4]

An alternative route to thermal cross-linking is provided by incorporation of the diacetylene group into the backbone.[6] This cross-linking group has been introduced into a variety of polymers.[7,8] It provides for especially high thermal stabilities in polysilylenes,[9] higher than when ethenylene groups are used for this purpose.[10] The diacetylene group is introduced here into a series of polycarboranylenesiloxane copolymers for the purpose of cross-linking and preparation of high-temperature elastomers with enhanced thermal stabilities.

Similar diacetylene-containing materials have been reported that contain carborane and disiloxane groups.[11] Upon curing, these materials exhibited plastic characteristics. Dilution of the diacetylene groups along the backbone resulted in a reduction of the glass transition temperature for the cured materials. However, even with a disiloxane:carborane:diacetylene ratio of 10:9:1, the $T_g$ was not reduced below room temperature and these copolymers were not rendered elastomeric upon curing. Lower glass transition temperatures can be achieved by replacement of the disiloxyl groups with trisiloxyl groups,[12] and also by increasing the average segment length between cross-links. The effect of these synthetic modifications on material properties are reported below for copolymers prepared from 1,5-dichlorohexamethyltrisiloxane, dilithio-*m*-carborane, and dilithiodiacetylene.

## Experimental Section

**Materials.** Reagents were purchased from Aldrich unless noted otherwise. *n*-Butyllithium (*n*-BuLi, 2.5 M solution in hexanes) was titrated to more precisely determine its concentration.[13] Tetrahydrofuran (THF, anhydrous, 99.9%), diethyl ether (anhydrous, 99.5%), and lithium diisopropylamide (LDA,

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2.0 M solution in heptane/THF/ethylbenzene) were used as received. *m*-Carborane (*m*-CB, Olin) was sublimed (220 mT). Hexachloro-1,3-butadiene ($C_4Cl_6$, 97%) was vacuum-distilled (220 mT, 49.5 °C). Note: $C_4Cl_6$ is toxic as are most other chlorinated reagents. 1,5-Dichlorohexamethyltrisiloxane (DCTS, Gelest, 95%) was vacuum-distilled over Mg turnings (400 mT, 31 °C). The latter two reagents were collected as clear liquids into round-bottom single-neck flasks with valved side arms, stored under argon, and sealed with rubber septa.

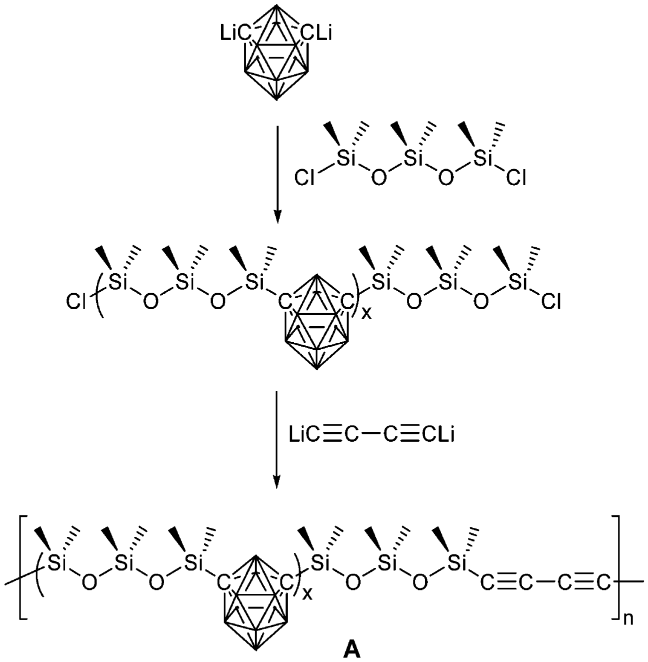
**Instrumentation.** Thermogravimetric analyses (TGA) were performed on a SDT 2960 simultaneous DTA-TGA analyzer. The differential scanning calorimetry (DSC) studies were performed on a DSC 2920 modulated DSC instrument. Unless otherwise mentioned, all thermal experiments (TGA and DSC) were carried out with heating rates of 10 °C/min and a nitrogen flow rate of 100 $cm^3$/min. Infrared (IR) spectra were obtained on a Nicolet Magna 750 Fourier transform infrared spectrometer. Solution-state $^1H$ and $^{13}C$ NMR spectra were acquired on a Bruker AC-300 spectrometer and referenced to the internal solvent peak (chloroform-*d* or $CDCl_3$). Solid-state $^1H$ NMR spectra were obtained on a Bruker DMX 500 using a triple-resonance MAS probe. The samples were packed in a 4-mm rotor which was loaded upside down in the stator to prevent it from spinning. $^1H$ NMR spectra of the static samples were acquired using single-pulse excitation with a 6-$\mu$s 90° pulse, a 100-kHz spectral width, 4.5-$\mu$s dead-time delay, 5-s recycle delay, and 4 scans. Gel permeation chromatography was conducted in THF (1 mL/min) at 303 K on three Waters Styragel columns (5-$\mu$m beads: HR 0.5; HR 1; HR 4) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector.

**Synthesis.** Glassware was baked at 120 °C for 24 h and then allowed to cool while dry argon passed through. All liquids were transferred with gastight syringes (Hamilton) preflushed 3 times with dry argon; needles were 20 gauge, 12-in. stainless steel. Unless otherwise noted, all syntheses were performed under an atmosphere of dry argon utilizing standard Schlenk techniques. The preparation of 1,4-dilithio-1,3-butadiyne (dilithiodiacetylene) was an adaptation of a literature procedure.[14] Note: Due to the exothermic nature of the reaction during the dilithiodiacetylene production, a strict adherence to the reaction conditions is highly recommended. It has been the experience, however, of the authors that the diacetylene unit is rather inert once incorporated into the polymer, undergoing cross-linking only upon heating above 200 °C for several hours.

Two sets of copolymers were prepared with the same overall molar ratios of trisiloxane (**S**) to carborane (**C**) to diacetylene (**D**) groups in the backbone. For both sets, the **S**:**C**:**D** ratios are 3:2:1, 5:4:1, and 10:9:1. The constituent groups were incorporated into linear polymers through a synthetic sequence that yielded either an alternating (**A**) or a block (**B**) copolymer with respect to the distribution of diacetylenes along the backbone. The copolymers are signified by their copolymer sequence (**A** or **B**) along with attending subscripts to identify the overall ratio of trisiloxane to carborane. For example, the alternating copolymer prepared with a **S**:**C**:**D** ratio of 3:2:1 is $\mathbf{A}_{3:2}$.

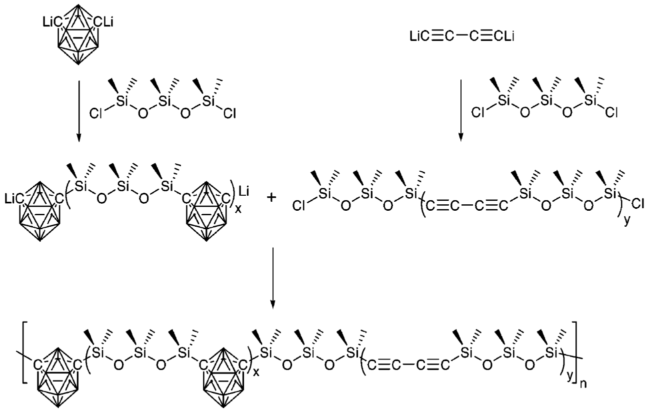
Both copolymer types were prepared with a previously established two-pot procedure. For the alternating copolymers (see Scheme 1), dichloro-terminated trisiloxane−carborane prepolymers were prepared in flask #1 and dilithiodiacetylene was prepared in flask #2; cannulation of the dilithiodiacetylene into flask #1 resulted in chain extension of the prepolymers to yield alternating copolymers in which the diacetylene groups are uniformly distributed along the backbone. For the block copolymers (see Scheme 2), dichloro-terminated trisiloxane−diacetylene (**S**−**D**) prepolymers were prepared in flask #1 and dilithio-terminated carborane−trisiloxane (**C**−**S**) prepolymers were prepared in flask #2; cannulation of the dichloro-terminated **S**−**D** prepolymer into flask #2 resulted in the formation of copolymers containing **S**−**D** and **C**−**S** blocks. Standard procedures are described below using quantities for a copolymer containing a trisiloxane-to-carborane ratio of 3:2.

**Scheme 1. Synthesis of Alternating Copolymers Containing Trisiloxane, Carborane, and Diacetylene Groups**



**A**

**Scheme 2. Synthesis of Block Copolymers Containing Carborane−Trisiloxane and Trisiloxane−Diacetylene Blocks**



**B**

*Alternating Copolymer with Trisiloxane−Carborane−Diacetylene Ratio of 3:2:1 ($\mathbf{A}_{3:2}$).* Flask #1: A 200-mL Kjeldahl reaction flask with a valved side arm and sealed with a rubber septum was evacuated and back-filled three times with argon. It was then placed on a balance and the rubber septum removed briefly enough to weigh *m*-carborane (0.57 g, 3.95 mmol) directly into the flask. A magnetic stir bar was inserted and the rubber septum was replaced. The assembly was then evacuated and back-filled three times with argon. Dry THF (1 mL) was transferred into the flask and the *m*-carborane dissolved to give a clear solution. The reaction flask was immersed in an ice bath and lithium diisopropylamide (LDA, 3.99 mL, 7.98 mmol) was added dropwise via a syringe. As the first drops hit the solution, they appeared to disperse and the deep orange color of LDA disappeared. As the addition proceeded, the clear solution became increasingly orange and turbid. After complete addition, the ice bath was removed. The reaction mixture was a thick slurry with a white precipitate. After stirring overnight, volatiles were removed with high

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vacuum and the solid residue was redissolved in fresh THF (5 mL) to give a clear deep orange solution. This solution was then cooled with an ice bath and 1,5-dichlorohexamethyltrisiloxane (1.61 mL, 5.92 mmol) was added dropwise. A white precipitate formed very quickly. The ice bath was removed and the reaction was allowed to proceed for about 5 h.

Flask #2: THF (3.50 mL) and *n*-butyllithium (3.13 mL, 2.52 M, 7.90 mmol) were transferred to a 50-mL Kjeldahl reaction flask with a valved side arm containing a magnetic stir bar and sealed with a rubber septum. The flask was then immersed in a dry ice/2-propanol bath. While stirring, hexachloro-1,3-butadiene (0.31 mL, 1.97 mmol) was added dropwise over 15 min, forming a blue, then purple, and then black solution. The dry ice/2-propanol bath was removed and the reaction mixture was warmed to room temperature with stirring over 4 h, resulting in the formation of a white precipitate.

Chain extension: Flask #1 was cooled with an ice bath. The contents of flask #2 were then cannulated into flask #1 (double-tipped needle, 18 gauge, 24 in.). Following the transfer, the remaining contents of flask #2 were rinsed three times with THF (4 mL/rinse) through the cannula into flask #1. The reaction was allowed to proceed overnight and the contents were then poured into a saturated $NH_4Cl$ solution (30 mL, aqueous) at 0 °C. The reaction flask was then rinsed with diethyl ether into the $NH_4Cl$ quench solution. The resulting two-phase mixture was transferred to a 250-mL separatory funnel and washed with a saturated $NH_4Cl$ (aq) solution until the pH was neutral and then two times with distilled $H_2O$. The dark organic phase was poured into an Erlenmeyer flask and dried over anhydrous $Na_2SO_4$. Filtration into a round-bottomed flask was followed by rotary evaporation and then exposure to reduced pressure at room temperature for 5 h. The crude product was a viscous brown paste (1.9 g, 100% yield): $^{13}C$ NMR ($\delta$, ppm in $CDCl_3$): 86.8, 85.1, 68.3, 1.85, 0.95, 0.83, 0.48. $^1H$ NMR ($\delta$, ppm in $CDCl_3$): 3.2−1.3 (carborane, 10 H, m), 0.29, 0.21, 0.14, 0.1. IR (neat, $cm^{-1}$): 2597 ($\nu_{B-H}$), 2071 ($\nu_{C\equiv C}$), 1262 ($\nu_{Si-C}$), 1059 ($\nu_{Si-O}$), 801.

*Block Copolymer with Trisiloxane−Carborane−Diacetylene Ratio of 3:2:1 (**B**$_{3:2}$).* Flask #1 involves production of trisiloxane−diacetylene blocks with an average degree of polymerization of 3: A flame-dried 250-mL Schlenk flask under argon was charged with 10 mL of dry THF and cooled to −78 °C (2-propanol/dry ice). *n*-BuLi (2.77 mL of 2.5 M in hexanes, 6.92 mmol, 4 equiv) was added slowly to the THF. After 10 min, $C_4Cl_6$ (0.27 mL, 1.73 mmol) was added dropwise over 15 min. The resulting gray-brown slurry was warmed to room temperature and stirred for 3 h. After this period, the mixture was cooled again to −78 °C and DCTS (0.68 mL, 3.46 mmol) was added dropwise via a gastight syringe. The mixture was then warmed to room temperature and stirred for 2 h, resulting in the formation of a large amount of a white precipitate (LiCl).

Flask #2 involves production of carborane−trisiloxane blocks of varying degrees of polymerization: In a 250-mL flame-dried Schlenk flask under argon, *m*-CB (0.50 g, 3.47 mmol) was dissolved in 1 mL of THF and cooled to −78 °C. LDA (3.50 mL, 7.01 mmol) was added dropwise to the solution, resulting in the formation of a reddish-orange solid. On warming of the mixture to room temperature, the solid redissolved in THF. The volatiles were then removed under vacuum. The residue was redissolved in 2 mL of THF and the mixture was cooled to 0 °C. To this solution, DCTS (0.34 mL, 1.73 mmol) was added dropwise via a gastight syringe. The resulting mixture was stirred for 3 h at room temperature.

Chain extension: The contents of flask #1 were cannulated into flask #2 and the mixture was stirred for 16 h. A few drops of DCTS were then added to the mixture and the stirring was continued for an additional hour. The mixture was then poured into 50 mL of a cold, saturated $NH_4Cl$ solution and extracted three times with 75 mL each of $Et_2O$. The $Et_2O$ extracts were combined, washed with 100 mL of brine, dried over anhydrous $Na_2SO_4$, filtered through a 1-in. pad of Celite, and the solvent was removed under vacuum. A dark brown viscous oil was obtained (1.9 g, 100% yield). $^{13}C$ NMR ($\delta$, ppm in $CDCl_3$): 86.8, 85.1, 68.3, 1.85, 0.95, 0.83, 0.48. $^1H$ NMR ($\delta$, ppm in $CDCl_3$): 3.2−1.3 (carborane, 10 H, m), 0.29, 0.21, 0.14, 0.1. IR (neat, $cm^{-1}$): 2597 ($\nu_{B-H}$), 2071 ($\nu_{C\equiv C}$), 1262 ($\nu_{Si-C}$), 1059 ($\nu_{Si-O}$), 801 ($\nu_{Si-O}$).

A similar procedure was followed for the syntheses of the remaining two block copolymers, **B**$_{5:4}$ and **B**$_{10:9}$, using the appropriate amounts of reagents as shown in Table 1.

**Table 1. Reactant Amounts for Block Copolymer Syntheses**

| | flask #1 (mmol) | | | flask #2 (mmol) | | |
|---|---|---|---|---|---|---|
| | $C_4Cl_6$ | *n*-BuLi | DCTS | *m*-CB | LDA | DCTS |
| **B**$_{3:2}$ | 1.73 | 6.92 | 3.46 | 3.47 | 7.01 | 1.74 |
| **B**$_{5:4}$ | 0.86 | 3.44 | 1.73 | 3.44 | 6.95 | 2.57 |
| **B**$_{10:9}$ | 0.38 | 1.52 | 0.76 | 3.44 | 6.91 | 3.03 |

## Results and Discussion

With use of the routes shown in Schemes 1 and 2, copolymers were prepared with the same overall ratio of trisiloxane (**S**) to carborane (**C**) to diacetylene (**D**) groups, but different copolymer sequences. Three alternating and three block copolymers were synthesized with **S**:**C**:**D** ratios of 3:2:1, 5:4:1, and 10:9:1, which represent materials with decreasing concentrations of cross-linkable diacetylene groups. Both synthetic procedures lead to almost quantitative yields (99−100%). In both methods, care must be taken to keep the reaction media as concentrated as possible to promote chain extension over cyclization. For example, in flask #1 of the alternating-copolymer synthesis, dilithiocarborane is prepared by the addition of lithium diisopropylamide to *m*-carborane in THF. However, before the dichlorosiloxane is added to form the dichloro-terminated trisiloxane−carborane prepolymers, the solvents (THF plus the heptane/THF/ethylbenzene in which the LDA is dissolved) are removed by high vacuum and the solid is redissolved in a minimal quantity of THF. Cyclization of carborane−siloxanes has been documented[3] and some evidence was observed here in the form of low (∼10%) char yields in thermogravimetric analysis of the alternating copolymers prepared before adding the concentration step to the synthetic procedure.

Infrared spectra contain absorptions characteristic of each of the three structural components in these copolymers. Carboranes are represented by the B−H stretch at 2597 $cm^{-1}$, diacetylenes by the C≡C stretch at 2071 $cm^{-1}$, and siloxanes by the Si−O stretch at 1059 $cm^{-1}$. Other absorptions include those due to C−H and Si−C groups in the siloxane units. Major peaks of the $^1H$ and $^{13}C$ NMR spectra are also characteristic of the three major segments of these polymers. Numerous minor peaks also appear in the NMR spectra and are attributed to a variety of end groups and the polydispersity of these relatively low-molecular-weight polymers. The carborane carbons appear at 68.3 ppm in the $^{13}C$ NMR spectra, indicating complete reaction (unreacted carborane carbons appear at 55 ppm).

Direct spectral evidence for the successful dilution of the diacetylene groups in the copolymer structure is provided by infrared spectra (see Figure 1). For each set of copolymers, the IR absorption intensities of diacetylene groups decrease with respect to that of the carborane groups as the **S**:**C**:**D** ratio goes from 3:2:1 to 10:9:1. Infrared spectra are shown in Figure 1 for the

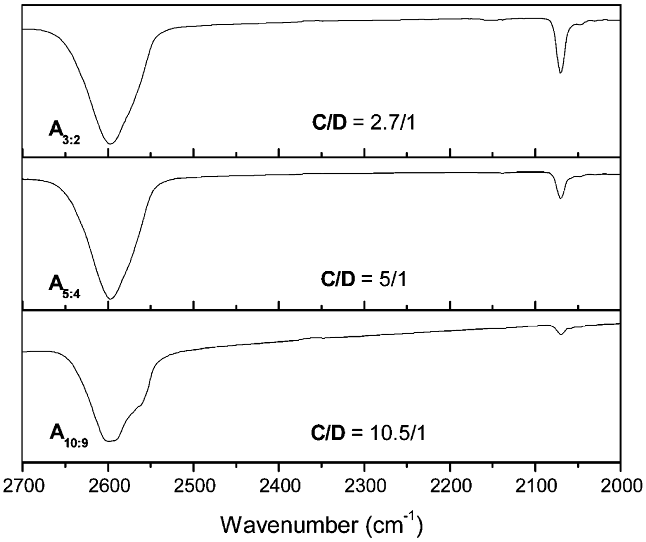

**Figure 1.** Selected region of the IR spectra for the alternating copolymers, diacetylene-containing polycarboranylenesiloxanes, with trisiloxane–carborane–diacetylene ratios of 3:2:1 ($\mathbf{A}_{3:2}$), 5:4:1 ($\mathbf{A}_{5:4}$), and 10:9:1 ($\mathbf{A}_{10:9}$). The diacetylene absorption (2071 cm$^{-1}$) decreases with respect to the carborane absorption (2597 cm$^{-1}$) in proceeding from $\mathbf{A}_{3:2}$ to $\mathbf{A}_{10:9}$. The **C**/**D** ratios refer to the absorption peak heights.

**Table 2. GPC Molecular Weights**

| copolymer | $M_n$ (kg/mol) | $M_w$ (kg/mol) |
|---|---|---|
| $\mathbf{A}_{3:2}$ | 4.3 | 6.6 |
| $\mathbf{A}_{5:4}$ | 3.3 | 5.4 |
| $\mathbf{A}_{10:9}$ | 5.2 | 8.6 |
| $\mathbf{B}_{3:2}$ | 3.4 | 6.2 |
| $\mathbf{B}_{5:4}$ | 2.9 | 4.3 |
| $\mathbf{B}_{10:9}$ | 4.1 | 6.7 |

alternating copolymer. Such spectra may be used to monitor the reaction of the diacetylene groups.

Molecular weights were determined by gel permeation chromatography using polystyrene standards and are presented in Table 2. For a given reactant ratio, the alternating copolymers exhibit slightly higher molecular weights than the block copolymers.

**Thermal Analysis.** The thermal properties of the copolymers were studied by differential scanning calorimetry (DSC). The DSC thermograms for the alternating and block copolymers are shown in Figures 2 and 3, respectively. All of the materials display an exotherm that begins around 275 °C, peaks above 350 °C, and extends to temperatures over 400 °C. This exotherm is attributed to reactions of the diacetylene groups. For a given copolymer type, the exotherm peak temperature and peak width increases with decreasing concentration of diacetylene groups. For the copolymers containing the lowest concentration of diacetylene groups ($\mathbf{A}_{10:9}$ and $\mathbf{B}_{10:9}$), very broad exotherms extend from 275 to 400 °C. These observations simply reflect the importance of the local concentration of reactive diacetylene groups on the ease of thermal activation.[15,16] When the local concentration is high (e.g., as in $\mathbf{A}_{3:2}$ and $\mathbf{B}_{3:2}$), the diacetylenes react at lower temperatures and over a narrower temperature range or time period. Further evidence for this local-concentration effect is seen when comparing the alternating copolymer sequence to that of the block copolymer. For a given **S**:**C**:**D** ratio, the exotherm peak temperature is about 10 °C lower for the block copolymer, in which the diacetylene groups are concentrated into the trisiloxane–diacetylene block. Local concentrations of diacetylene groups are also higher in the diacetylene-containing polycarboranylenesiloxanes consisting of disiloxane instead of trisiloxane units along the backbone.[11] For a given **S**:**C**:**D** ratio, the disiloxane-containing materials exhibit exotherm peak temperatures about 10 °C lower than those displayed by the trisiloxane-containing block copolymers reported here.

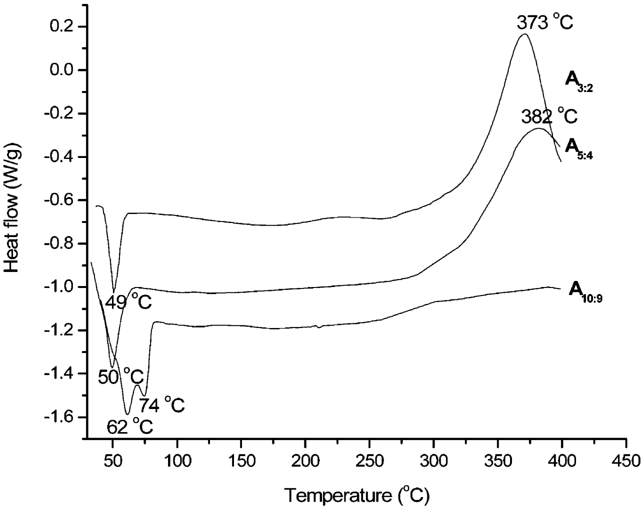

**Figure 2.** DSC thermograms for the alternating copolymers, diacetylene-containing polycarboranylenesiloxanes, with trisiloxane to carborane to diacetylene ratios of 3:2:1 ($\mathbf{A}_{3:2}$), 5:4:1 ($\mathbf{A}_{5:4}$), and 10:9:1 ($\mathbf{A}_{10:9}$). 10 °C/min in $N_2$.

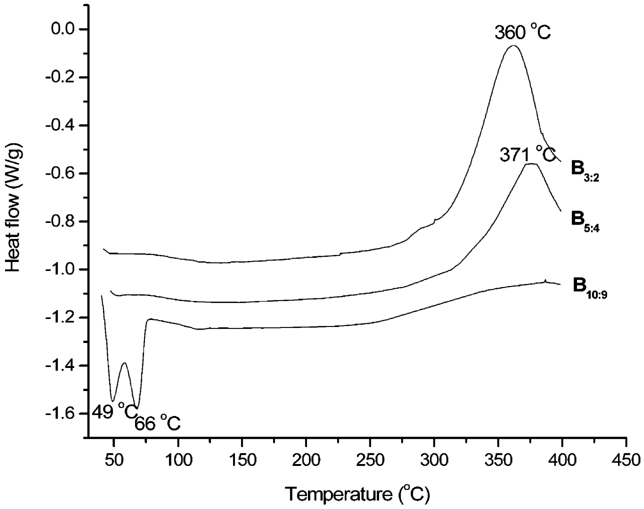

**Figure 3.** DSC thermograms for the block copolymers, diacetylene-containing polycarboranylenesiloxanes, with trisiloxane to carborane to diacetylene ratios of 3:2:1 ($\mathbf{B}_{3:2}$), 5:4:1 ($\mathbf{B}_{5:4}$), and 10:9:1 ($\mathbf{B}_{10:9}$). 10 °C/min in $N_2$.

Each of the alternating copolymers, as prepared, is a solid and exhibits a melting endotherm that peaks between 49 and 74 °C (see Figure 2). However, melting is only observed for the block copolymer with the lowest diacetylene concentration ($\mathbf{B}_{10:9}$), which shows two endotherms (see Figure 3). The alternating copolymer with the lowest concentration of diacetylene groups ($\mathbf{A}_{10:9}$) also exhibits multiple endotherms, while the other two alternating copolymers display a single endotherm.

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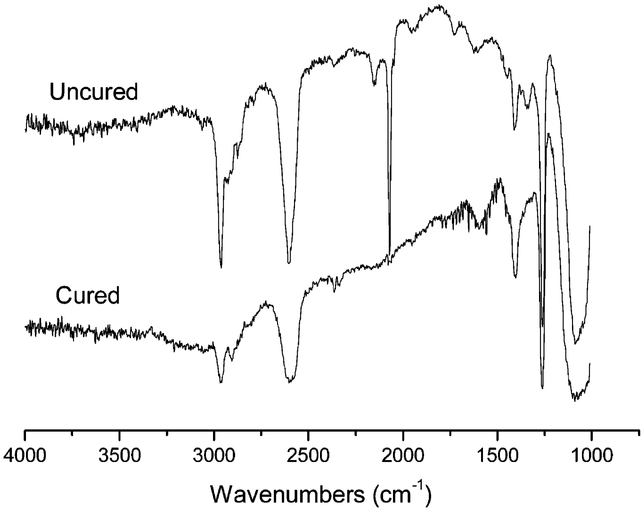

**Figure 4.** IR spectra for the block copolymer, diacetylene-containing polycarboranylenesiloxane, with a trisiloxane to carborane to diacetylene ratio of 3:2:1 (**$B_{3:2}$**) before and after thermal treatment in $N_2$ at 250 °C for 30 min and 400 °C for 2 h.

Thus, the copolymer sequence has a noticeable effect on the chain-packing characteristics of these materials. This effect is not as pronounced for the materials containing the lowest diacetylene concentration (**$A_{10:9}$** and **$B_{10:9}$**).

After thermal treatments, the copolymers were no longer soluble in organic solvents, confirming that the diacetylene reactions yielded cross-linked thermosets. Each copolymer was exposed to a cure cycle in $N_2$ for 30 min at 250 °C and then for 2 h at 400 °C. Curing was monitored with IR spectroscopy and deemed complete by the disappearance of the diacetylene absorption at 2071 cm$^{-1}$ (see Figure 4). The mechanism by which the diacetylenes cross-link includes several possibilities: a 1,2-addition, a 1,4-addition, and a cyclic trimerization. The absence of an asymmetric acetylene stretch (between 2100 and 2000 cm$^{-1}$) in the IR spectra of the cured polymers rules out a simple 1,2-addition reaction. However, a definitive determination of the cross-linking mechanism in these polymers has not yet been achieved.

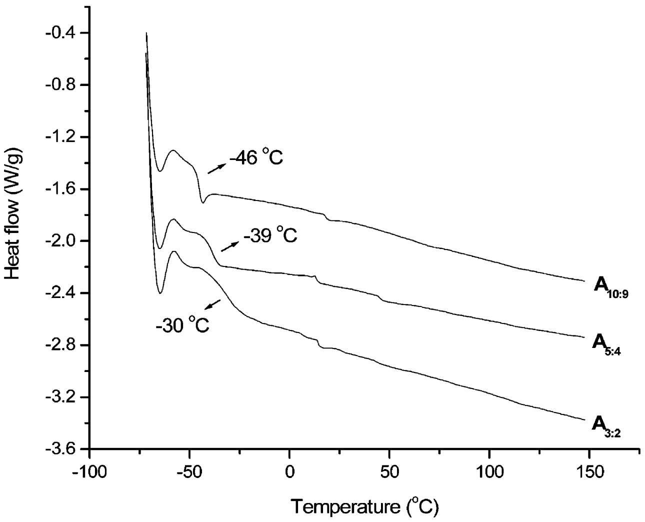

**Figure 5.** DSC thermograms for the thermally cured alternating copolymers, diacetylene-containing polycarboranylenesiloxanes.

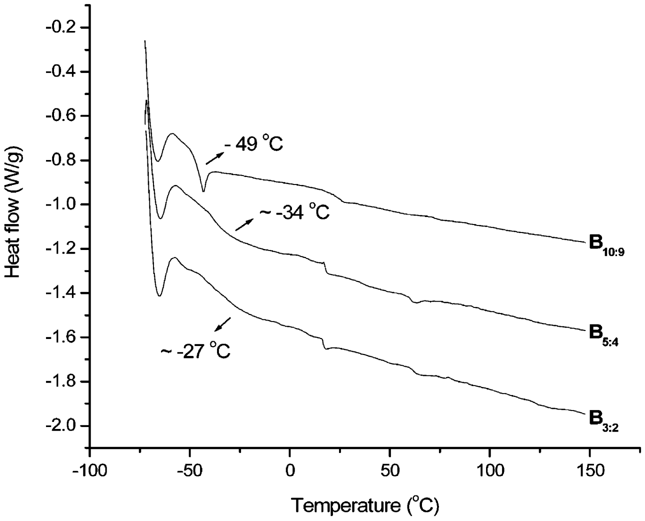

**Figure 6.** DSC thermograms for the thermally cured block copolymers, diacetylene-containing polycarboranylenesiloxanes.

**Table 3. Thermal Properties of Cured Copolymers**

| copolymer | $T_g$ (°C) | $T_d$$^a$ (°C) | char yield (%) | oxidative wt gain of char (%) |
|---|---|---|---|---|
| **$A_{3:2}$** | −30 | 620 | 70 | 1.3 |
| **$A_{5:4}$** | −39 | 575 | 65 | 4 |
| **$A_{10:9}$** | −46 | 555 | 46 | 8 |
| **$B_{3:2}$** | −27 | 623 | 74 | 1.3 |
| **$B_{5:4}$** | −34 | 580 | 70 | 4 |
| **$B_{10:9}$** | −49 | 558 | 52 | 8 |

[a] Temperature of 10% weight loss in $N_2$.

The glass transitions ($T_g$) of the cured networks were determined from the DSC thermograms shown in Figures 5 and 6 for the alternating and block copolymers, respectively. $T_g$ values are shown in Table 3 for each copolymer. Minor transitions also appear for the alternating copolymers between 13 and 19 °C and at 46 °C, and for the block copolymers around 18 °C and between 60 and 65 °C. In general, as the diacetylene concentration increases, yielding an enhancement in cross-link density, the $T_g$ increases. The $T_g$'s are well-defined for the two copolymers with lowest concentration of diacetylene groups (**$A_{10:9}$** and **$B_{10:9}$**). In fact, these glass transitions (−46 °C for **$A_{10:9}$** and −49 °C for **$B_{10:9}$**) are similar to the $T_g$ of −50 °C reported for the un-cross-linked polycarboranylenesiloxane containing *m*-carborane and hexamethyltrisiloxane units.[5] For the alternating copolymers with higher diacetylene concentrations (**$A_{5:4}$** and **$A_{3:2}$**), the glass transition remains relatively well-defined. However, the block copolymers with higher diacetylene concentrations (**$B_{5:4}$** and **$B_{3:2}$**) exhibit broadened glass transitions that reflect a larger distribution of segment lengths between cross-links as compared to the samples with sharper glass transitions.

Solid-state $^1H$ wide-line NMR was used to further examine the glass transition in these cured copolymers. Figure 7 shows the $^1H$ NMR line width measured as a function of temperature for the alternating and block copolymers containing the highest concentration of diacetylene groups (**$A_{3:2}$** and **$B_{3:2}$**). Note the sharp transition for the alternating copolymer and broadened transition for the block copolymer, consistent with the DSC results. Thus, a single $T_g$ is difficult to identify in

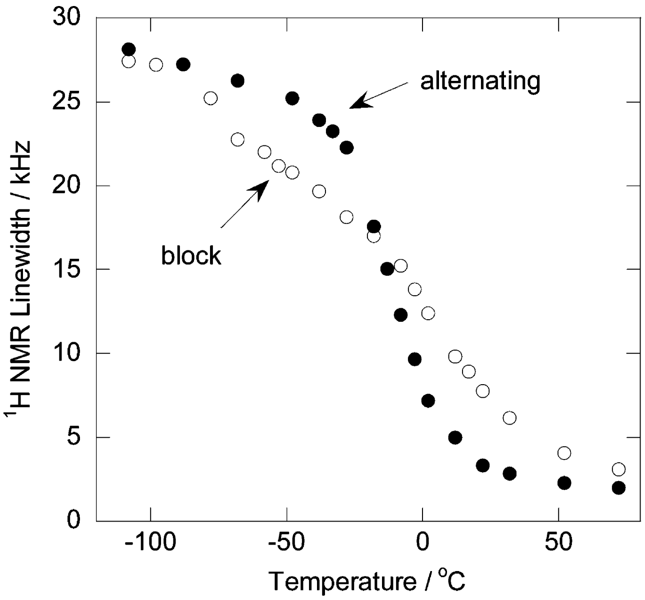

**Figure 7.** $^1$H solid-state NMR static-sample line widths versus temperature for the cured alternating (●) and block (○) copolymers, diacetylene-containing polycarboranylenesiloxanes, containing trisiloxane−carborane−diacetylene ratios of 3:2:1 (**A**$_{3:2}$ and **B**$_{3:2}$).

the data for the block copolymers. If the inflection point is taken as the glass transition for the alternating copolymer, the NMR $T_g$ is about −13 °C, which is higher than the −30 °C value determined from DSC simply because these NMR measurements are sensitive to higher frequencies (∼kHz) than the DSC measurements.

The thermal stabilities of the cured copolymers were analyzed gravimetrically by heating to 1000 °C in $N_2$. Before the TGA analysis, the copolymers were cured using the same protocol as that used for the DSC studies. The results are shown in Table 3. For a given copolymer type, the degradation temperatures ($T_d$) and char yields increase as the diacetylene content increases. Higher char yields are typically observed for higher cross-link densities.[17] For a given **S**:**C**:**D** ratio, the char yields were about 4−6% higher for the block copolymers as compared to the alternating copolymers. The degradation temperatures, on the other hand, were not significantly different between the two copolymer types for a given **S**:**C**:**D** ratio. Defined here as the temperature of 10% weight loss, the degradation temperatures were measured in both $N_2$ and air. While the weight loss was continuous above 800 °C in $N_2$, the weight change subsided in air as oxidative weight gain became important.

After heating to 1000 °C in $N_2$, the resulting chars were then subjected to thermo-oxidative analysis by thermal exposure to 1000 °C in air. Each material exhibited oxidative weight gain (see Table 3) that was correlated with the overall composition and not at all to copolymer sequence. The greatest oxidative weight gain (8%) was exhibited by the materials containing the lowest concentration of diacetylene groups (**A**$_{10:9}$ and **B**$_{10:9}$) and therefore lowest cross-link density. The weight gain was most pronounced above 800 °C, with the samples adding 90% of their total weight gain above this temperature. The high oxidative stability of these materials makes them potentially useful as protective coatings for organic fibers.

## Conclusions

Substitution of disiloxane by trisiloxane moieties in the diacetylene-containing carboranylenesiloxanes[11] is observed to render elastomeric cured networks. Variations in the copolymer sequence are found to cause discernible differences in the thermal properties of the resultant networks prepared with trisiloxane−carborane−diacetylene ratios of 3:2:1 and 5:4:1. The results from this study have revealed avenues for the systematic control of the material properties of polycarboranylenesiloxanes by judicious choice of the constituent siloxane, cross-linker (such as diacetylene), and the cross-linker placement in the network precursors.

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